

DETERMINATION OF AROMATICS IN HEATING OILS AND DIESEL FUELS BY SUPERCRITICAL FLUID CHROMATOGRAPHY

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INTRODUCTION

The presence of high quantities of aromatic compounds in middle distillate fuels causes problems for refiners and users because of the sooting propensity of such oils. Distillate fuels containing a high proportion of aromatic compounds are being produced due to the increased use of non-conventional crudes and of lower cost blending components to maximize product yield.

The method normally used in refineries for determining aromatics in oils is ASTM D 1319, the fluorescent indicator adsorption (FIA) method (1). The method uses inexpensive equipment and is simple to perform; however, it does have some limitations. The procedure is lengthy and results depend upon the operator's ability to distinguish between the colored bands, which can be difficult for colored samples. Problems have been reported with variations in dye composition and availability of the proper grade and activity of silica gel (2). Finally, the scope of the method excludes samples with final boiling points greater than 315°C.

The purpose of the present work was to develop a simple, inexpensive and precise method to determine aromatics content in heating oils and diesel fuels. It was desired that the method be applicable to samples boiling as high as 400°C, and that it be suitable for use in refinery control laboratories.

Mass spectrometry and nuclear magnetic resonance may be used for aromatics determination, but both require expensive instrumentation and highly trained operators. They are therefore unsuitable for routine refinery use.

Many methods based on high performance liquid chromatography (HPLC) have been employed for saturates and aromatics determination. Some examples are those reported by Suatoni and Swab (3), Alfredson (4) and Cookson et al (5). Generally these methods are characterized by good separation, analysis times of less than 10 minutes, and are not limited to low boiling samples. Their main disadvantage is the specificity of the usual ultraviolet (UV) and refractive index (RI) detectors, which require extensive calibration using either model compounds similar to those in the samples being analyzed, or fractions prepared from the actual samples by open column chromatography.

Two detectors thought to be preferable to the RI and UV, because of their relative uniformity of response for hydrocarbon types over a wide range of carbon numbers, are the dielectric constant (DC) detector and the flame ionization detector (FID). This uniformity of response greatly simplifies the calibration procedure. Hayes and Anderson (6) used a DC detector in conjunction with conventional HPLC

employing Partisil columns and n-butylchloride as the mobile phase to determine saturates, monoaromatics and polyaromatics in fuel distillates.

The FID presents a problem when used with conventional HPLC because of interference from commonly used solvents. Norris and Rawdon (2) have successfully coupled supercritical fluid chromatography (SFC) with FID using carbon dioxide as the mobile phase and a silica column coated with silver nitrate to determine saturates, olefins and aromatics in gasolines. Schwartz and Brownlee (7) also employed SFC/FID to determine paraffins, olefins and aromatics in gasolines employing a silica column with sulfur hexafluoride as the mobile phase.

In SFC the mobile phase is a highly compressed gas (8) with excellent solvating properties. This condition is achieved above the critical temperature and pressure of the mobile phase. Generally the density of the fluid and hence its solvating ability is increased by either increasing the pressure or decreasing the temperature. This will usually result in a loss of selectivity within a homologous series, but can be advantageous when class separations (saturates, aromatics) are desired over a wide molecular weight range. An SFC system is easily coupled to an FID with little interference from the mobile phase fluid since it rapidly desolvates before entering the detector (9).

In the present work the effects of temperature, pressure and stationary phase on the SFC/FID determination of aromatics in middle distillate fuels were investigated. The FID response to both saturates and aromatics isolated from several actual samples was determined. Results were compared to those obtained by the FIA method, and the possibilities of using SFC/FID for determining aromatics on the basis of number of rings was investigated.

EXPERIMENTAL

Instrumentation

A Varian model 8500 syringe pump was used to pressurize the carbon dioxide in the chromatographic column. Inlet pressures were between 3250 and 4200 psi (22,400 and 28,900 kPa). To facilitate filling of the pump with liquefied gas, two alternate methods were used. One employed a Lauda model K4R circulator bath to keep the syringe pump cooled. The other employed a cylinder of carbon dioxide prepressurized to 1200 psi with helium which allowed the pump to be filled without cooling (10). A Shimadzu model GC-8A gas chromatograph equipped with an FID contained the chromatographic column. The GC was run isothermally at temperatures ranging from 35 to 90°C; the temperature of the detector was 400°C. A Rheodyne valve model 7520 equipped with a 0.2 μ L internal sample loop mounted on the exterior of the gas chromatograph was employed to introduce the sample onto the column. A Spectra-Physics model 4290 computing integrator was used for the collection and reduction of the data.

Columns and Restrictors

All columns were 250mm x 2.1mm ID (Alltech Associates). The following stationary phases were employed: 5 μ silica adsorbosphere, 5 μ cyano, 5 μ amino, and 20% AgNO₃ on 5 μ silica. The restrictors were flexible fused silica capillary tubing attached to the column with a 0.4mm 40% graphite ferrule with a low dead volume fitting. Either 50mm of 10 μ ID tubing inserted approximately 30mm into the FID, or 130mm of 20 μ ID tubing inserted approximately 90mm into the FID, as close as possible to the flame, was used. The latter arrangement was found to eliminate "spiking", a common problem in SFC (10).

Chemicals and Calibration Materials

Fisher Scientific ACS grade carbon disulfide (CS_2) was used for dilution of the samples. A modification of the column chromatographic procedure of Sawatzky et al (11) was used for the preparation of saturates and aromatics fractions from several actual samples. The saturates fraction was eluted from the silica-alumina column with n-pentane and the aromatics with toluene. Following careful air drying to remove the solvent these fractions were used for checking the FID response factors.

RESULTS AND DISCUSSION

Saturates-Aromatics Separation

- A. Effect of Temperature: Retention time data, expressed as capacity factors, for a series of model compounds are shown in the first two columns of Table 1 for the silica stationary phase, mobile phase pressure of 3600 psi and temperatures of 90 and 35°C. The capacity factor, k , is defined by:

$$k = (t_R - t_0) / t_0$$

where t_R is the retention time of the given model compound, and t_0 is the retention time of a compound not retained by the column which in this case is the impurity peak in the CS_2 solvent. At both temperatures, the saturates span a much smaller range of k values than do the aromatics. However, it can be seen that at 35°C the saturates as a group are better separated from the monoaromatics. For example at this temperature C_{30} has a lower k value than does benzene, but at 90°C C_{20} and toluene have approximately the same k values. The boiling points of toluene and C_{30} correspond approximately with the lowest initial boiling point and the highest final boiling point (as determined by gas chromatographic simulated distillation) of all middle distillate samples studied in the present work.

The dramatic improvement in saturates-aromatics separation upon decreasing the oven temperature is shown for an actual sample by the chromatograms in Figure 1. The sharp initial eluting peak is due to the saturates. At 35°C there is almost baseline separation between the saturates and the monoaromatic group of peaks. An added advantage of operating at the lower temperature is the shorter retention times, which would result in shorter analysis times per sample. For example, phenanthrene elutes in 11 min. at 90°C compared to 6 min. at 35°C. This can be attributed to increased density of the supercritical CO_2 at the lower temperature, which increases its solvating ability (8).

- B. Effect of Pressure: Data are not shown, but there was some improvement in separation between saturates and aromatics at 90°C when the pressure was increased from 3250 to 3600 psi, presumably due to the increased density of the CO_2 . At 35°C, however, there was virtually no change in the separation over the pressure range of 3000 and 4200 psi.
- C. Effect of Stationary Phase: Grizzle and Sablotny (12) employed HPLC with two aminosilane columns in series and hexane/methylene chloride as the mobile phase to separate saturates and aromatics. Lundanes and Greibrokk (13) reported that a silver-impregnated silica column was required to obtain complete separation of saturates and aromatics by SFC using CO_2 . Based on these studies we investigated three other columns or combinations in an attempt to improve upon the separation between saturates and aromatics. The data obtained at a pressure of 3600 psi and temperature of 35°C are shown in

Table 1. It can be seen that the separation using the silica/cyano (Si/CN) combination is not as good as that of the silica at the same temperature. C_{30} and xylene have the same k value using the Si/CN, whereas C_{30} has a smaller k value than xylene with the silica alone. For the amino (NH_2) column the separation between saturates and aromatics is much poorer; in this case C_{30} has the same k value as hexamethylbenzene. From the limited number of compounds run, it appears that the series combination of silica/20% $AgNO_3$ on silica (Si/Ag) is no better than silica at 90°C. It is concluded that of the stationary phases studied in our SFC system, the best saturates-aromatics separation is obtained using a 5 μ silica column.

Calibration

In order to check FID response factors for saturates and aromatics, some calibration studies were carried out. The calibration curves were determined using saturates and aromatics fractions prepared from four middle distillate samples using the procedure reported by Sawatzky et al (11). Recoveries of material from the column ranged from 81 to 99 wt%, indicating the loss of some lower boiling components. The SFC chromatograms of one of the samples and of its separate fractions using the silica column at a pressure of 3250 psi and temperature of 90°C, are shown in Figure 2. The relatively high degree of purity of each fraction implies that the separations by column chromatography and SFC are similar making the fractions suitable for calibration purposes.

The calibration curves obtained over a broad range of concentration using CS_2 solutions of the saturates and aromatics fractions are shown in Figure 3. The data points were fitted to the line: $y = A \cdot x$. The response factors as given by the slopes of each line differ by only 5%. Differences of this order of magnitude were reported for GC/FID work on model compounds (14), from which it was concluded the response factors are more or less equivalent.

Curvature was noted in the saturates response above approximately 100×10^6 area counts, whereas the aromatics response was linear to 300×10^6 area counts. The likely reason for this behavior is that the FID becomes saturated above a certain concentration. The saturates, which have a much sharper peak, saturate the detector at a lower sample size than do the aromatics. Because of this non-linear behavior, it was necessary to reduce the concentration of sample reaching the FID by dilution. CS_2 was chosen as the solvent because of its low FID response. It was found for all samples in this study that dilution by a factor of ten was sufficient to bring the saturates into the linear range.

Because of the close agreement between saturates and aromatics response for fractions obtained from actual samples, it was decided that the integrated area percentages may be used directly to quantitate saturates and aromatics provided that samples are diluted such that the components are within the linear range of the detector and that a small correction is made for the area of the impurity peak from the CS_2 .

Repeatability and Accuracy

The wt% aromatics values were obtained from analyses of duplicate (1:10) dilutions in CS_2 of each of 22 samples of heating oils and diesel fuels. Standard deviations ranged from 0 to 1.4 wt%. A pooled standard deviation value of 0.4 wt% was calculated from all data using the formula given by Snedecor and Cochran (15). According to ASTM C 670-81 (16) the standard deviation is multiplied by the factor 2.83 to obtain a repeatability. For the present data this repeatability statement is as follows: "Duplicate measurements by the same operator should be considered

suspect if they differ by more than 1.1 wt% 19 times out of 20*. This repeatability compares favorably with that reported for the FIA method (1).

These particular repeatability measurements were carried out by a chemical technologist with one year of gas chromatographic experience. Three days were required for this individual to become familiar with the operation of the instrument and to perform the analyses. This indicates the relative simplicity of the technique, and suggests its suitability for use in refinery control laboratories.

The accuracy of the method could not be determined using actual samples since the absolute aromatics contents were not known. An indication of the accuracy, however, was made using known mixtures of hexadecane and naphthalene in CS₂. The differences between actual and measured values ranged from 0 to 1 wt%.

Comparison to the FIA Method

Despite its disadvantages, FIA is the most widely used standard method in the oil industry for aromatics determination. For this reason it was used as a basis for comparison of the present SFC/FID results. This comparison is shown by the plot in Figure 4. A linear regression of the data, indicated by the solid line in Figure 4, yielded a correlation coefficient of 0.9018. The 95% confidence interval for this regression is given by the dashed curves. The consistent bias of all but three of the points to higher values by SFC/FID (slope=0.97) probably reflects the fact that the output of FIA is in vol% whereas that for SFC/FID is in wt%. This has also been indicated in the work of Norris and Rawdon (2).

There are two possible explanations for the three samples whose points lie outside the confidence limits. First, these samples yielded olefins values by FIA greater than 3 vol%. High concentration of olefins do interfere with the separation between saturates and aromatics on a silica column (17), which might result in the lower aromatics values by SFC. Secondly, two of these three samples contain components boiling well above 315°C which makes the FIA results questionable for these samples.

Classification of Aromatics by Number of Rings

The capacity factor data for the silica column at both 90 and 35°C shown in Table 1 in general indicate a grouping of the aromatics according to number of rings. The only significant overlap occurs between the monoaromatics, hexamethylbenzene and octahydroanthracene, and the diaromatic compounds. It is suspected that these monoaromatics overlap because of the large amount of pi electron delocalization over the ring structures. For the model compounds considered in the present work good separation is obtained between the diaromatics and polyaromatics.

Stationary phases other than silica, such as amino-modified silica, have been employed to separate polycyclic aromatic hydrocarbons by HPLC (12,19) and by SFC (20). Our SFC data using a series combination of Si/CN stationary phases, shown in Table 1, indicate marginally better separation between mono- and diaromatics compared to silica alone, but poorer saturates-monoaromatics separation. The NH₂ column provides the best separation between mono- and diaromatics, but very poor saturates-monoaromatics separation (the k value for C₃₀ is greater than most of the monoaromatic compounds as seen from Table 1). Finally, with the series combination of Si/Ag, the separation among aromatic types appears to be no better than the silica column. It is concluded that, of the stationary phases studied in the present work, a single silica column would be the one preferred for quantitation of aromatics according to number of rings.

CONCLUSIONS

A method employing SFC with FID, similar to that reported by Norris and Rawdon for the analysis of gasolines (2), has been developed for the determination of aromatics in middle distillate fuels. The method is simple, employs relatively inexpensive equipment, gives good repeatability and provides results which correlate well with those obtained by FIA. The SFC method is not affected by sample color, appears to be applicable to samples with final boiling points as high as 450°C and should be suitable for use in a refinery control laboratory. Initial indications are that the determination of aromatics according to the number of rings can be accomplished by SFC/FID.

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TABLE 1

Comparison of Capacity Factors of Some Model Compounds Using Different Stationary Phases*

| Compound ----- | Silica 90°C ----- | Silica 35°C ----- | Si/CN 35°C ----- | NH ₂ 35°C ----- | Si/Ag 35°C ----- |
|--------------------------------|-------------------------|-------------------------|------------------------|----------------------------------|------------------------|
| Saturates: | | | | | |
| N-pentane | - | - | - | - | 0.00 |
| N-hexane | 0.00 | - | - | - | - |
| 3-Methylheptane | 0.02 | - | - | - | - |
| N-decane | 0.04 | 0.00 | - | - | - |
| Cyclohexane | 0.04 | - | - | - | - |
| Dimethylcyclohexane | 0.05 | 0.04 | - | 0.00 | - |
| Hexadecane | 0.11 | - | - | - | - |
| Decalin | 0.13 | 0.05 | - | - | - |
| Eicosane (C ₂₀) | 0.18 | 0.04 | - | - | 0.17 |
| Triacontane (C ₃₀) | - | 0.09 | 0.15 | 1.12 | 0.26 |
| Monoaromatics: | | | | | |
| Benzene | 0.16 | 0.17 | - | - | - |
| Toluene | 0.19 | 0.17 | - | - | - |
| 3-Ethyltoluene | 0.24 | 0.16 | - | - | - |
| O-xylene | 0.26 | 0.20 | 0.15 | 0.27 | 0.26 |
| Indane | 0.33 | 0.25 | - | - | - |
| 1-Phenyldodecane | 0.39 | 0.24 | - | - | - |
| Tetralin | 0.41 | - | 0.27 | 0.62 | - |
| Hexamethylbenzene | 0.69 | - | 0.47 | 1.12 | - |
| Octahydroanthracene | 0.80 | - | 0.54 | 1.62 | - |
| Diaromatics: | | | | | |
| Naphthalene | 0.53 | 0.37 | 0.41 | 1.12 | 0.49 |
| 2-Methylnaphthalene | 0.56 | - | 0.47 | 1.27 | - |
| Thianaphthalene | 0.56 | - | 0.47 | 1.27 | - |
| Biphenyl | 0.70 | - | 0.44 | 1.46 | - |
| Acenaphthalene | 0.80 | - | 0.65 | - | - |
| Bibenzyl | 0.92 | - | 0.57 | - | - |
| Polyaromatics: | | | | | |
| Fluorene | 1.02 | - | - | - | - |
| Dibenzothiophene | 1.16 | - | - | - | - |
| Anthracene | 1.22 | - | - | - | - |
| Phenanthrene | 1.27 | 0.85 | 1.15 | 4.85 | 1.08 |
| Thianthrene | 1.76 | - | - | - | - |
| Fluoranthene | 1.82 | - | 1.78 | - | - |
| Pyrene | 1.92 | - | - | - | - |
| Chrysene | - | 1.89 | - | - | - |

* All runs were carried out at a pressure of 3600 psi.

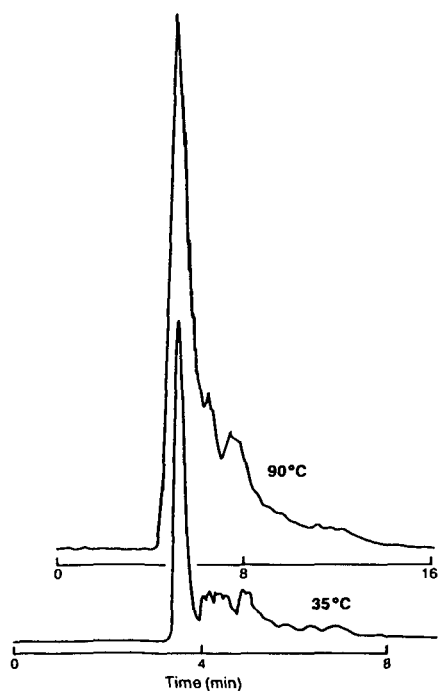


FIGURE 1: SFC chromatograms of a middle distillate sample at temperatures of 90 and 35 °C using a silica column and pressure of 3600 psi.

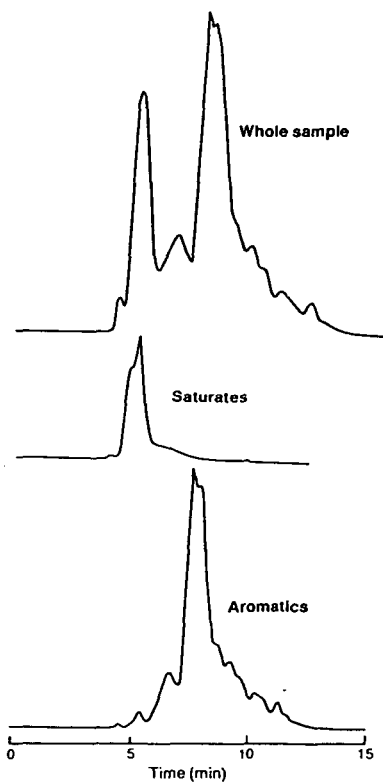


FIGURE 2: SFC chromatograms obtained at 90°C and 3250 psi of a whole middle distillate sample and of its saturates and aromatics fractions separated by column chromatography.

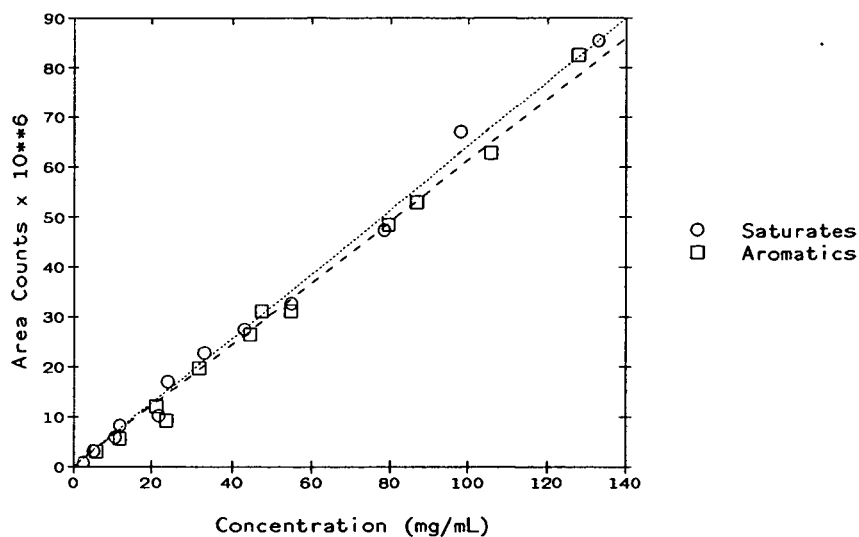


FIGURE 3: SFC calibration curves using saturates and aromatics fractions separated from middle distillates by column chromatography.

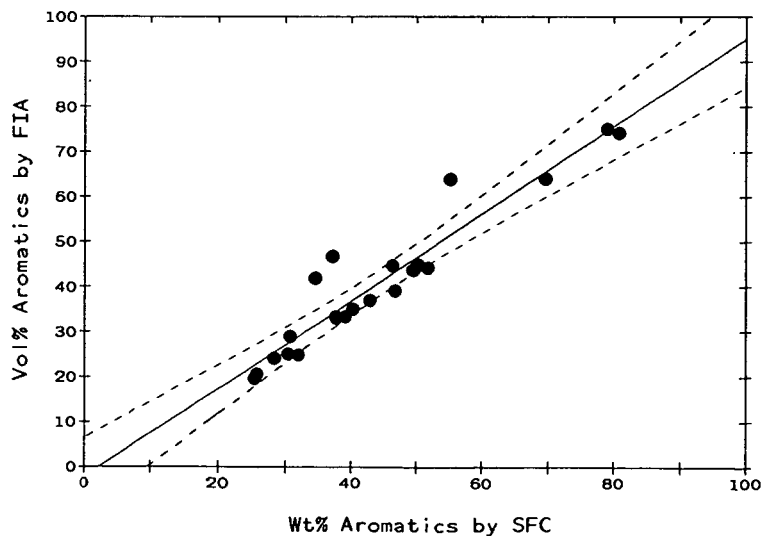


FIGURE 4: Comparison of aromatics content of middle distillates by SFC and FIA.